Published in final edited form as:

Curr Opin Electrochem. 2023 April ; 38: . doi:10.1016/j.coelec.2023.101228.

3D printing for customized carbon electrodes

Yuanyu Chang,

Qun Cao,

B. Jill Venton

Department of Chemistry, University of Virginia, Charlottesville, VA, 22904

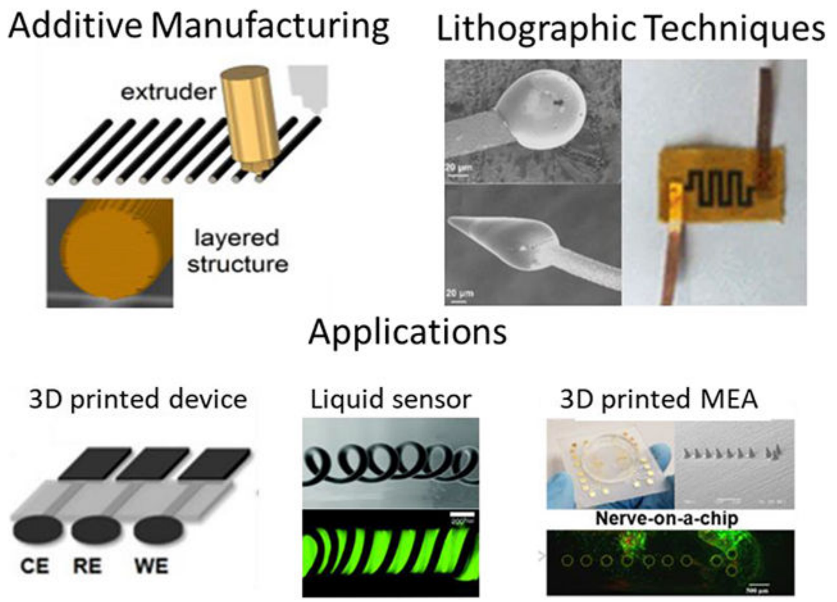
Abstract

Traditional carbon electrodes are made of glassy carbon or carbon fibers and have limited shapes. 3D printing offers many advantages for manufacturing carbon electrodes, such as complete customization of the shape and the ability to fabricate devices and electrodes simultaneously. Additive manufacturing is the most common 3D printing method, where carbon materials are added to the material to make it conductive, and treatments applied to enhance electrochemical activity. A newer form of 3D printing is 2-photon lithography, where electrodes are printed in photoresist via laser lithography and then annealed to carbon by pyrolysis. Applications of 3D printed carbon electrodes include nanoelectrode measurements of neurotransmitters, arrays of biosensors, and integrated electrodes in microfluidic devices.

Graphical Abstract

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



1. Introduction

In recent years, electrochemistry has joined the 3D printing revolution, with new methods to design electrodes including additive manufacturing and lithography.[1] Traditional carbon electrodes were typically made from glassy carbon or carbon fibers, with cylindrical or disk geometries.[2] 3D printing offers the opportunity to make electrodes in a completely different manner: by designing them from the bottom up. Thus, the shape is customizable, because the designs are drawn in a computer-assisted drawing program rather than based on the physical shape of the material.[3]

3D printing started with additive manufacturing of plastics, and adding carbon materials makes the material conductive.[4,5] A newer form of 3D printing that allows smaller electrodes to be printed is 2-photon lithography.[6,7] Electrodes are printed in photoresist via laser lithography, where only the small voxel where the lasers meet is polymerized, and the electrode is annealed by pyrolysis to make a carbon electrode. This review focuses on examples of additive manufacturing and 2-photon lithography manufacturing processes, outlining the limitations and advantages of 3D printing carbon electrodes. Finally, we highlight some of the advantages of 3D printing in making devices and custom electrodes and discuss applications of 3D printed carbon electrodes.

2. Methods for 3D printing Carbon Electrodes

2.1 Additive Manufacturing

The most common method of making 3D-printed carbon electrodes is additive manufacturing, where a mixture of conductive polymer and carbon/graphene is extruded. An early example of this work was 3D printing high-impact polystyrene with carbon nanofibers or graphite to determine lead ions by differential pulse voltammetry (Figure 1A).[8] Polylactic acid (PLA) is now the preferred conductive polymer as it has a low printing temperature and is more biocompatible. Pumera's group pioneered PLA/graphene electrodes as detectors for picric acid or ascorbic acid (Figure 1B).[9] Kolivoška's group used fused deposition modeling (FDM) 3D printing to print polylactic acid with carbon black (CB) electrodes (Figure 1C).[10] Munoz's group used a 3D printing pen instead of a desktop printer to print PLA/CB electrodes with similar properties and showed a good performance for 2,4,6-trinitrotoluene (TNT) sensing via square-wave voltammetry (Figure 1D).[11] However, the 3D printing pens are limited in precision.[12]

One issue with 3D-printed carbon electrodes is that the electrochemical reactions can be slow, and thus treatments are applied to increase kinetics. Applying a high positive voltage for anodic activation increases the oxygen functional groups[2] and defect sites, which enhance the detection of neurotransmitters such as dopamine and serotonin.[13] Chemical treatments, such as NaOH, dimethylformamide (DMF), or acetone, also improve the conductivity and kinetics by cleaning the PLA and etching the carbon surface.[14] Moreover, combining electrochemical and chemical treatment enhances the signal even more;[15,16] for example, applying 2.5 V to 3D printed graphene electrodes in DMF significantly enhances the electrochemical performance compared to DMF only.[17] Coating metal particles on the printed electrodes also improves the performance,[18] such as gold nanoparticles that enhance the conductivity.[19] Biological pretreatment with proteinase K enhances the 3D printed PLA/graphene electrode response for ferricyanide.[20] In addition, reagentless treatments also improve electrochemical performance,[21,22] such as thermal activation to significantly enhance the electron transfer rate.[23] Overall, pretreatment of the 3D-printed carbon electrodes to enhance the performance is essential for electrochemical sensing.

2.2 2-Photon Lithography

Two-photon lithography is a new method to make 3D-printed electrodes. A substrate is covered with photoresist, which is polymerized by lasers. Only specific voxels polymerize where the two lasers produce photons in the same place; thus the spatial resolution is on the order of 1 μm.[24] When the unpolymerized photoresist is washed away, the remaining structure is not electroactive, but it can be annealed to form pyrolyzed glassy carbon by heating to high temperatures.[7,25] The pyrolysis procedure also shrinks the structure 3-5 fold. Thus, the electrode features are as small as 500 nm, which is smaller than the resolution of the printer.

The Venton group pioneered making freestanding 2-photon lithography printed electrodes for neurochemical applications.[7,25] Figure 2A shows the process flow for the fabrication of 3D-printed carbon electrodes by direct laser writing. The electrodes were printed on small metal wires; the printed structures were 180 μm spheres or cones which shrunk to about 60 μm when they were pyrolyzed. Surface features, such as spikes, could be printed with a diameter of 1 μm or less. To make nanoelectrodes, the niobium wire substrate was etched to 1 μm or less and smaller, tapered tips were printed that were submicron after annealing.[25] The Keller group fabricated pyrolytic carbon microelectrodes with improved conductivity by selective direct laser writing (Figure 2B).[26] The Li group fabricated strain sensors with high sensitivity and stability by direct laser writing of graphene (Figure 2C).[27]

Two-photon lithography offers potential upsides of customized shapes, but there are design limitations. One issue is that tapered tips tend to curl during annealing. Figure 3A gives examples of structural deformation for high aspect ratio geometry. The structure is stable with an apex angle about 20 degrees,[25] but the tip curls with higher aspect ratios (Figure 3A, b-c). To avoid curling, the nanolattice and printing density can be adjusted,[28-31] enabling a feature size of pyrolytic carbon down to 100 nm.[32,33] To fabricate high aspect ratio structures, the structure can be mounted with spatial restrictions-such as making a needle tip connected to a base that would limit deformation.[34]

Another issue is that of shadows and attachment to the wire. Shapes generally need to be printed from the bottom up, as there is a shadow effect and the lasers cannot print under an object. Figure 3B illustrates a vertical setup, where the metal wires are bent vertically to the stage and the printing axis (z-axis) is the same as the alignment of the wire, so the printed structure attaches to the metal wire from the beginning and there is no shadow. However, it is very challenging to bend the metal wires to a perfectly vertical position, and any deviation from the vertical direction results in asymmetrical printing. In the future, a mold to assist the vertical mounting of metal wires would be helpful. An easier fabrication method is a horizontal set-up of the stage (Fig. 3C). The wires are laid on the wafer with the tip hanging off the end, allowing batch fabrication without specialized mounting. However, the printing process starts on the underside of the wire but the structure does not contact the metal wire until printing is half done (Figure 3C, bottom panel). When the structure is not attached to the wire, it floats in the liquid photoresist and can move out of its intended position. Figure 3D describes a possible solution: printing a small cylinder attached to the wire first as an anchor, and then printing the desired structure upward. Figure 3E shows how the shadow is created under the wire, since the laser power cannot pass through the metal wire; smaller tips have less shadow effect.

3. Advantages and applications of 3D printing

3.1 Integrated Fabrication of Electrodes and Devices.

One advantage of 3D printing is that the electrodes can be printed into devices as they are made. 3D printers with dual extrusion properties embed conductive carbon electrodes into nonconductive polymeric devices, with rapid prototyping and customization on demand. For example, the Kokkinos group designed a single-step fabrication of an integrated 3-electrode 3D printed device (Figure 4A).[35] The Bergamini group utilized 3D-printed electrodes as a new platform for immunoassays (Figure 4B).[36] The Martin group fabricated a 3D-printed microfluidic chip with directly embedded electrodes (Figure 4C).[37] The Rajaraman group combined 3D-printed microelectrode arrays and 3D-printed nerve-on-a-chip as a biocompatible device for cell culture *in vitro* (Figure 4D).[38] The Coltro group also fabricated an 8-electrode device used for adrenaline analysis.[39] While integration is easiest with additive manufacturing, silicon probes with multiple functionalities could be printed with 2-photon lithography. Thus, one of the main advantages of 3D printing is that it facilitates the integration of electrodes into devices.

3.2 Customized and flexible electrode design

Traditional carbon-based electrodes are fabricated as disk or cylindrical shapes but 3D printing allows customization of the electrode shape. For example, the Yan group utilized 3D printing for a tunable and stretchable CNT electrode with excellent resistance stability (Figure 5A).[40] The Therriault group fabricated a multifunctional helical liquid sensor by solvent-cast 3D printing. The multi-walled CNT composite enhanced the electrical conductivity and the helical shape traps the solution for sensitive liquid sensing (Figure 5B).[41] Moreover, a flexible 3D piezoelectric nanocomposite containing polyurethane and carbon black was also fabricated by 3D printing for pressure sensing (Figure 5C).[42] The Liu group utilized direct laser writing to create porous graphitic structures and fabricated flexible piezoresistive sensor arrays (Figure 5D).[43] A new method called stereolithography (SLA) with pyrolysis uses a laser beam to cure a printed photopolymer resin layer-by-layer, constructing a 3D shape.[44] This method was used to make freestanding carbon electrodes with complex designs, like a cubic mesh. The Venton lab fabricated freestanding carbon-based microelectrodes by 2-photon lithography 3D printing for neurochemical applications, with cone, sphere, and nanospike modified designs.[7] Moreover, carbon-based nanodisk electrodes were also fabricated via 3D printing combined with other treatments and applied for dopamine detection in the *Drosophila* brain.[25]

3.3 Batch manufacturing of more complex electrodes

One of the advantages of 3D printing carbon electrodes is that they can be batch fabricated reproducibly. Ironically, it is also easy to prototype, as designs are relatively easy to produce in software and then can be printed quickly. Once a design is finalized, the printer will reproducibly print that design hundreds or thousands of times. The field is not yet at the manufacturing scale, but initial papers showed the printing design with 2-photon lithography showed a 1% variance when printing a sphere.[7] However, the shape was not the exact size of the design, so differences in design and actual printing need to be considered before batch manufacturing.

Future applications of customized sensors

Customized electrodes combined with different devices have been broadly applied in multiple fields for electrochemical detection, from neurochemistry to metal sensing to immunosensing. For example, a tunable and stretchable carbon electrode would be a good sensor for gut measurement as 3D printing technology improves.[46] A freestanding electrode with nanoscale resolution will also enable direct monitoring of synaptic neurotransmitter release in the future. 3D printed carbon microelectrode arrays (MEA) can be applied for multiple site detection in tissues or cell culture with good biocompatibility. Microfluidic devices with 3D-printed carbon MEAs or biosensors provide the opportunity for rapid, multistep analysis on one device. Finally, 3D printed electrodes provide an opportunity for fundamental studies by customizing the electrode, for example, to study thin layer cell behavior.[3] Thus, 3D-printed electrodes have the potential to revolutionize numerous biological and environmental monitoring fields to enable new and better electrochemical analysis.

Acknowledgement

The research from the Venton lab was funded by NIH R01NS125663

References

(1). Blyweert P; Nicolas V; Fierro V; Celzard A 3D Printing of Carbon-Based Materials: A Review. Carbon 2021, 183, 449–485. 10.1016/j.carbon.2021.07.036.

(2). McCreery RL Advanced Carbon Electrode Materials for Molecular Electrochemistry. Chem. Rev 2008, 108 (7), 2646–2687. 10.1021/cr068076m. [PubMed: 18557655]

(3). Shao Z; Chang Y; Venton BJ Carbon Microelectrodes with Customized Shapes for Neurotransmitter Detection: A Review. Anal. Chim. Acta 2022, 1223, 340165. 10.1016/j.aca.2022.340165. [PubMed: 35998998]

(4). Agarwala S; Goh GL; Yap YL; Goh GD; Yu H; Yeong WY; Tran T Development of Bendable Strain Sensor with Embedded Microchannels Using 3D Printing. Sens. Actuators Phys 2017, 263, 593–599. 10.1016/j.sna.2017.07.025.

(5). Zolfagharian A; Khosravani MR; Kaynak A Fracture Resistance Analysis of 3D-Printed Polymers. Polymers 2020, 12 (2), 302. 10.3390/polym12020302. [PubMed: 32024315]

(6). Abaddi MA-; Sasso L; Dimaki M; Svendsen WE Fabrication of 3D Nano/Microelectrodes via Two-Photon-Polymerization. Microelectron. Eng 2012, 98, 378–381. 10.1016/j.mee.2012.07.015.

(7). Yang C; Cao Q; Puthongkham P; Lee ST; Ganesana M; Lavrik NV; Venton BJ 3D-Printed Carbon Electrodes for Neurotransmitter Detection. Angew. Chem. Int. Ed 2018, 57 (43), 14255–14259. 10.1002/anie.201809992.

(8). Rymansaib Z; Iravani P; Emslie E; Medvidović-Kosanović M; Sak-Bosnar M; Verdejo R; Marken F All-Polystyrene 3D-Printed Electrochemical Device with Embedded Carbon Nanofiber-Graphite-Polystyrene Composite Conductor. Electroanalysis 2016, 28 (7), 1517–1523. 10.1002/elan.201600017.

(9). Manzanares Palenzuela CL; Novotný F; Krupička P; Sofer Z; Pumera M 3D-Printed Graphene/Polylactic Acid Electrodes Promise High Sensitivity in Electroanalysis. Anal. Chem 2018, 90 (9), 5753–5757. 10.1021/acs.analchem.8b00083. [PubMed: 29658700]

(10)*. Vaněčková E; Bouša M; Nováková Lachmanová Š; Rathouský J; Gál M; Sebechlebská T; Kolivoška V 3D Printed Polylactic Acid/Carbon Black Electrodes with Nearly Ideal Electrochemical Behaviour. J. Electroanal. Chem 2020, 857, 113745. 10.1016/j.jelechem.2019.113745. This paper used fused deposition modelling 3D printing to fabricate carbon based electrode and the electrode showed ideal electrochemical performance after activation. This work indicated that 3D printed electrode has electrochemical properties equal to conventional electrodes.

(11). Cardoso RM; Rocha DP; Rocha RG; Stefano JS; Silva RAB; Richter EM; Muñoz RAA 3D-Printing Pen versus Desktop 3D-Printers: Fabrication of Carbon Black/Polylactic Acid Electrodes for Single-Drop Detection of 2,4,6-Trinitrotoluene. Anal. Chim. Acta 2020, 1132, 10–19. 10.1016/j.aca.2020.07.034. [PubMed: 32980099]

(12). Abdalla A; Patel BA 3D Printed Electrochemical Sensors. Annu. Rev. Anal. Chem 2021, 14 (1), 47–63. 10.1146/annurev-anchem-091120-093659.

(13). Shao Z; Wilson L; Chang Y; Venton BJ MPCVD-Grown Nanodiamond Microelectrodes with Oxygen Plasma Activation for Neurochemical Applications. ACS Sens. 2022. 10.1021/acssensors.2c01803.

(14). Cardoso RM; Kalinke C; Rocha RG; dos Santos PL; Rocha DP; Oliveira PR; Janegitz BC; Bonacin JA; Richter EM; Munoz RAA Additive-Manufactured (3D-Printed) Electrochemical Sensors: A Critical Review. Anal. Chim. Acta 2020, 1118, 73–91. 10.1016/j.aca.2020.03.028. [PubMed: 32418606]

(15). Cao Q; Lucktong J; Shao Z; Chang Y; Venton BJ Electrochemical Treatment in KOH Renews and Activates Carbon Fiber Microelectrode Surfaces. Anal. Bioanal. Chem 2021, 413 (27), 6737–6746. 10.1007/s00216-021-03539-6. [PubMed: 34302181]

(16). Rocha DP; Squissato AL; da Silva SM; Richter EM; Munoz RAA Improved Electrochemical Detection of Metals in Biological Samples Using 3D-Printed Electrode: Chemical/Electrochemical Treatment Exposes Carbon-Black Conductive Sites. Electrochimica Acta 2020, 335, 135688. 10.1016/j.electacta.2020.135688.

(17). Browne MP; Novotný F; Sofer Z; Pumera M 3D Printed Graphene Electrodes' Electrochemical Activation. ACS Appl. Mater. Interfaces 2018, 10 (46), 40294–40301. 10.1021/acsami.8b14701. [PubMed: 30398834]

(18)*. Ghosh K; Ng S; Iffelsberger C; Pumera M Inherent Impurities in Graphene/Polylactic Acid Filament Strongly Influence on the Capacitive Performance of 3D-Printed Electrode. Chem. – Eur. J 2020, 26 (67), 15746–15753. 10.1002/chem.202004250. [PubMed: 33166037] This work characterized how the impurities in 3D printing fabrication influence the electrode properties. The metal-based impurities enhanced the 3D printed electrode capacity and this is important for the electrode manufacturing designs.

(19). Foo CY; Lim HN; Mahdi MA; Wahid MH; Huang NM Three-Dimensional Printed Electrode and Its Novel Applications in Electronic Devices. Sci. Rep 2018, 8 (1), 7399. 10.1038/s41598-018-25861-3. [PubMed: 29743664]

(20). Manzanares-Palenzuela CL; Hermanova S; Sofer Z; Pumera M Proteinase-Sculptured 3D-Printed Graphene/Polylactic Acid Electrodes as Potential Biosensing Platforms: Towards Enzymatic Modeling of 3D-Printed Structures. Nanoscale 2019, 11 (25), 12124–12131. 10.1039/C9NR02754H. [PubMed: 31211311]

(21). Cruz MA; Ye S; Kim MJ; Reyes C; Yang F; Flowers PF; Wiley BJ Multigram Synthesis of Cu-Ag Core–Shell Nanowires Enables the Production of a Highly Conductive Polymer Filament for 3D Printing Electronics. Part. Part. Syst. Charact 2018, 35 (5), 1700385. 10.1002/ppsc.201700385.

(22). Gnanasekaran K; Heijmans T; van Bennekom S; Woldhuis H; Wijnia S; de With G; Friedrich H 3D Printing of CNT- and Graphene-Based Conductive Polymer Nanocomposites by Fused Deposition Modeling. Appl. Mater. Today 2017, 9, 21–28. 10.1016/j.apmt.2017.04.003.

(23). Novotný F; Urbanová V; Plutnar J; Pumera M Preserving Fine Structure Details and Dramatically Enhancing Electron Transfer Rates in Graphene 3D-Printed Electrodes via Thermal Annealing: Toward Nitroaromatic Explosives Sensing. ACS Appl. Mater. Interfaces 2019, 11 (38), 35371–35375. 10.1021/acsami.9b06683. [PubMed: 31525017]

(24). Malinauskas M; Farsari M; Piskarskas A; Juodkazis S Ultrafast Laser Nanostructuring of Photopolymers: A Decade of Advances. Phys. Rep 2013, 533 (1), 1–31. 10.1016/j.physrep.2013.07.005.

(25)*. Cao Q; Shin M; Lavrik NV; Venton BJ 3D-Printed Carbon Nanoelectrodes for In Vivo Neurotransmitter Sensing. Nano Lett. 2020, 20 (9), 6831–6836. 10.1021/acs.nanolett.0c02844. [PubMed: 32813535] This study used lithographic printing techniques and FIB to fabricate carbon nanoelectrodes and successfully applied them for in vivo dopamine detection in fly brains. The ability to make nanoelectrodes could help direct synapse measurements in the future.

(26)*. Ludvigsen E; Pedersen NR; Zhu X; Marie R; Mackenzie DMA; Emnéus J; Petersen DH; Kristensen A; Keller SS Selective Direct Laser Writing of Pyrolytic Carbon Microelectrodes in Absorber-Modified SU-8. Micromachines 2021, 12 (5), 564. 10.3390/mi12050564. [PubMed: 34067628] This paper used direct laser writing to batch fabricate pyrolytic carbon electrodes with high resolution and flexible designs.

(27). Liu W; Huang Y; Peng Y; Walczak M; Wang D; Chen Q; Liu Z; Li L Stable Wearable Strain Sensors on Textiles by Direct Laser Writing of Graphene. ACS Appl. Nano Mater 2020, 3 (1), 283–293. 10.1021/acsanm.9b01937.

(28). Crook C; Bauer J; Guell Izard A; Santos de Oliveira C; Martins de Souza e Silva J; Berger JB; Valdevit L Plate-Nanolattices at the Theoretical Limit of Stiffness and Strength. Nat. Commun 2020, 11 (1), 1–11. 10.1038/s41467-020-15434-2. [PubMed: 31911652]

(29). Zhang X; Wang Y; Ding B; Li X Design, Fabrication, and Mechanics of 3D Micro-/Nanolattices. Small 2020, 16 (15), 1–19. 10.1002/smll.201902842.

(30). Zhang X; Vyatskikh A; Gao H; Greer JR; Li X Lightweight, Flaw-Tolerant, and Ultrastrong Nanoarchitected Carbon. Proc. Natl. Acad. Sci. U. S. A 2019, 116 (14), 6665–6672. 10.1073/pnas.1817309116. [PubMed: 30886098]

(31). Vyatskikh A; Delalande S; Kudo A; Zhang X; Portela CM; Greer JR Additive Manufacturing of 3D Nano-Architected Metals. Nat. Commun 2018, 9 (1), 1–8. 10.1038/s41467-018-03071-9. [PubMed: 29317637]

(32). Seniutinas G; Weber A; Padeste C; Sakellari I; Farsari M; David C Beyond 100 nm Resolution in 3D Laser Lithography — Post Processing Solutions. Microelectron. Eng 2018, 191, 25–31. 10.1016/j.mee.2018.01.018.

(33). Bauer J; Schroer A; Schwaiger R; Kraft O Approaching Theoretical Strength in Glassy Carbon Nanolattices. Nat. Mater 2016, 15 (4), 438–443. 10.1038/nmat4561. [PubMed: 26828314]

(34). Cardenas-Benitez B; Eschenbaum C; Mager D; Korvink JG; Madou MJ; Lemmer U; De Leon I; Martinez-Chapa SO Pyrolysis-Induced Shrinking of Three-Dimensional Structures Fabricated by Two-Photon Polymerization: Experiment and Theoretical Model. Microsyst. Nanoeng 2019, 5 (1), 1–13. 10.1038/s41378-019-0079-9. [PubMed: 31057928]

(35). Katseli V; Economou A; Kokkinos C Single-Step Fabrication of an Integrated 3D-Printed Device for Electrochemical Sensing Applications. Electrochem. Commun 2019, 103, 100–103. 10.1016/j.elecom.2019.05.008.

(36)*. Martins G; Gogola JL; Budni LH; Janegitz BC; Marcolino-Junior LH; Bergamini MF 3D-Printed Electrode as a New Platform for Electrochemical Immunosensors for Virus Detection. Anal. Chim. Acta 2021, 1147, 30–37. 10.1016/j.aca.2020.12.014. [PubMed: 33485583] They developed an immunosensing device for diagnosis of Hantavirus diseases by 3D printing. The sensor construction does not require pretreatment and the strategy could be applied for other viral disease detection.

(37). Castiaux AD; Currens ER; Scott Martin R Direct Embedding and Versatile Placement of Electrodes in 3D Printed Microfluidic-Devices. Analyst 2020, 145 (9), 3274–3282. 10.1039/D0AN00240B. [PubMed: 32242194]

(38). Kundu A; McCoy L; Azim N; Nguyen H; Didier CM; Ausaf T; Sharma AD; Curley JL; Moore MJ; Rajaraman S Fabrication and Characterization of 3D Printed, 3D Microelectrode Arrays for Interfacing with a Peripheral Nerve-on-a-Chip. ACS Biomater. Sci. Eng 2021, 7 (7), 3018–3029. 10.1021/acsbiomaterials.0c01184. [PubMed: 34275292]

(39). Silva-Neto HA; Dias AA; Coltro WKT 3D-Printed Electrochemical Platform with Multi-Purpose Carbon Black Sensing Electrodes. Microchim. Acta 2022, 189 (6), 235. 10.1007/s00604-022-05323-4.

(40). Wei H; Li K; Liu WG; Meng H; Zhang PX; Yan CY 3D Printing of Free-Standing Stretchable Electrodes with Tunable Structure and Stretchability. Adv. Eng. Mater 2017, 19 (11), 1700341. 10.1002/adem.201700341.

(41). Guo S; Yang X; Heuzey M-C; Therriault D 3D Printing of a Multifunctional Nanocomposite Helical Liquid Sensor. Nanoscale 2015, 7 (15), 6451–6456. 10.1039/C5NR00278H. [PubMed: 25793923]

(42). Tao R; Shi J; Granier F; Moeini M; Akbarzadeh A; Therriault D Multi-Material Fused Filament Fabrication of Flexible 3D Piezoelectric Nanocomposite Lattices for Pressure Sensing and Energy Harvesting Applications. Appl. Mater. Today 2022, 29, 101596. 10.1016/j.apmt.2022.101596.

(43). Luo S; Hoang PT; Liu T Direct Laser Writing for Creating Porous Graphitic Structures and Their Use for Flexible and Highly Sensitive Sensor and Sensor Arrays. Carbon 2016, 96, 522–531. 10.1016/j.carbon.2015.09.076.

(44). Rezaei B; Pan JY; Gundlach C; Keller SS Highly Structured 3D Pyrolytic Carbon Electrodes Derived from Additive Manufacturing Technology. Mater. Des 2020, 193, 108834. 10.1016/j.matdes.2020.108834.

(45). Abdalla A; Patel BA 3D-Printed Electrochemical Sensors: A New Horizon for Measurement of Biomolecules. Curr. Opin. Electrochem 2020, 20, 78–81. 10.1016/j.coelec.2020.04.009.

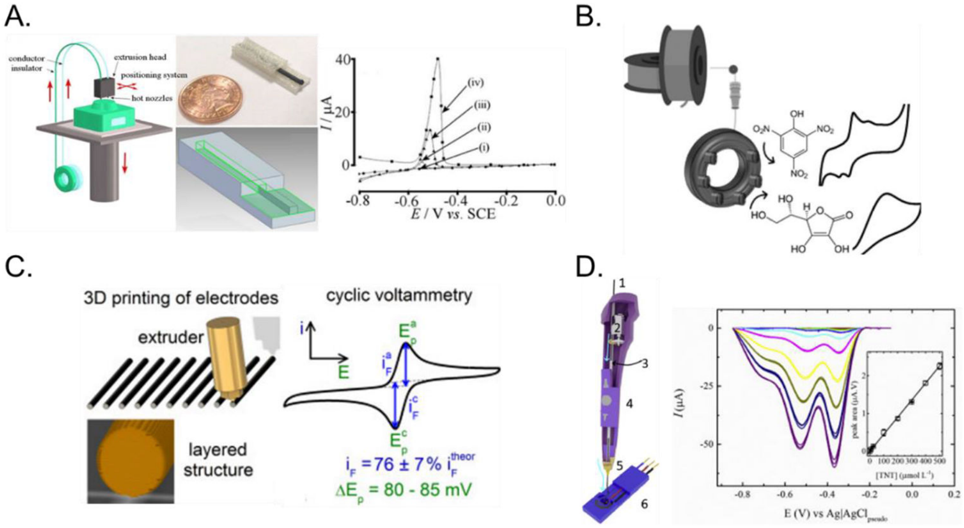


Figure 1.

Examples of additive manufacturing. (A) Directly 3D printed polystyrene/CNF/graphite composite electrode for Pb^{2+} sensing in aqueous solution (i-iv on the right represents different ion concentrations).[8] (B) PLA/Graphene for ascorbic acid and picric acid detection.[9] (C) PLA/Carbon black electrodes fabricated by FDM. The CV is $Ru(acac)_3$ detection.[10] (D) 3D printing pen printed PLA/CB electrode for TNT measurement via square-wave voltammetry.[11] Panels reprinted by permission from: Panel A Wiley, Panel B American Chemical Society, Panels C, D: Elsevier.

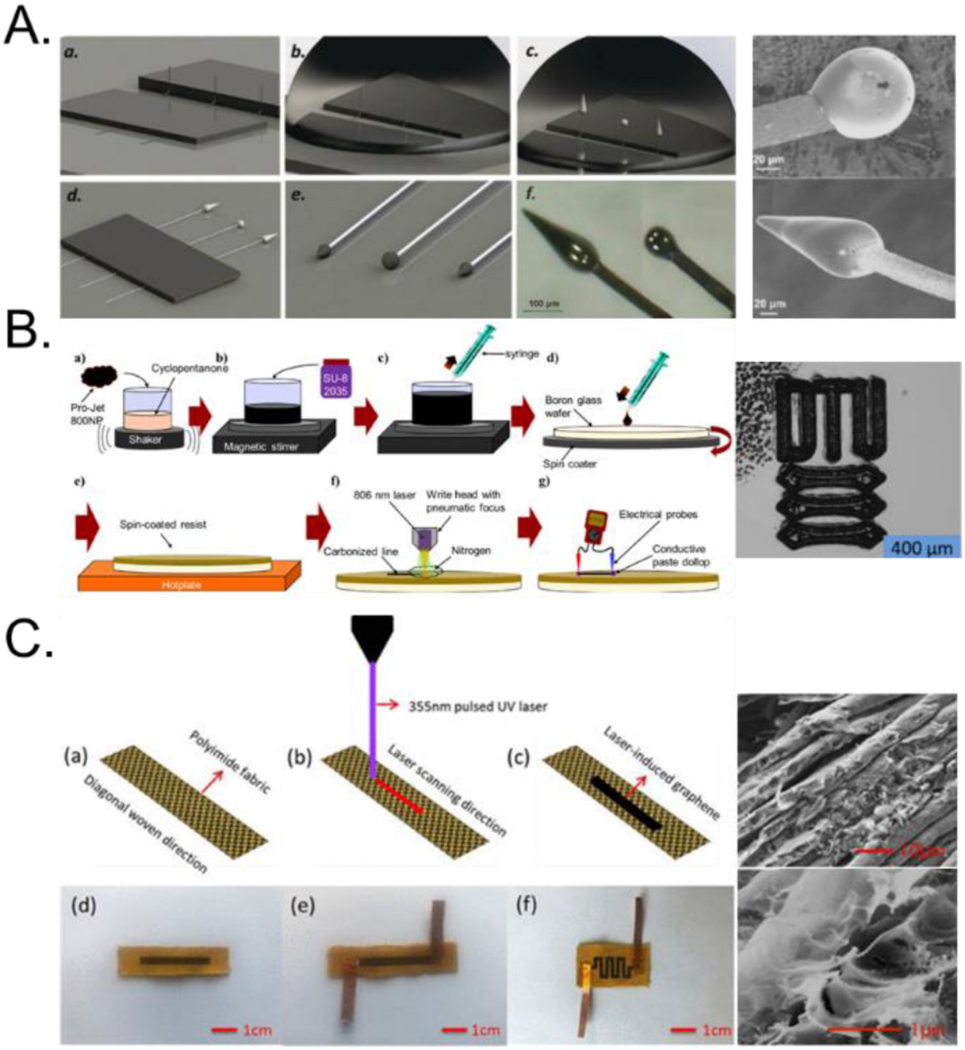


Figure 2.

Electrode fabrication by direct laser writing. (A) Left (a-f): Process flow for the fabrication of 3D-printed carbon electrodes. Right: SEM of the printed carbon microelectrodes.[7] (B) Left (a-g) Overview of pyrolytic carbon microelectrodes fabrication by selective direct laser writing. Right: The logo of the Technical University of Denmark (DTU) was written using 20 mW power and 0.3 mm/s scan speed.[26] (C) Left: Steps of direct laser writing of graphene. Right: Zoom in SEM figures of the printed sensor.[27] Reprinted by permission from, Panel A: Wiley, Panel B MDPI, Panel C: American Chemical Society.

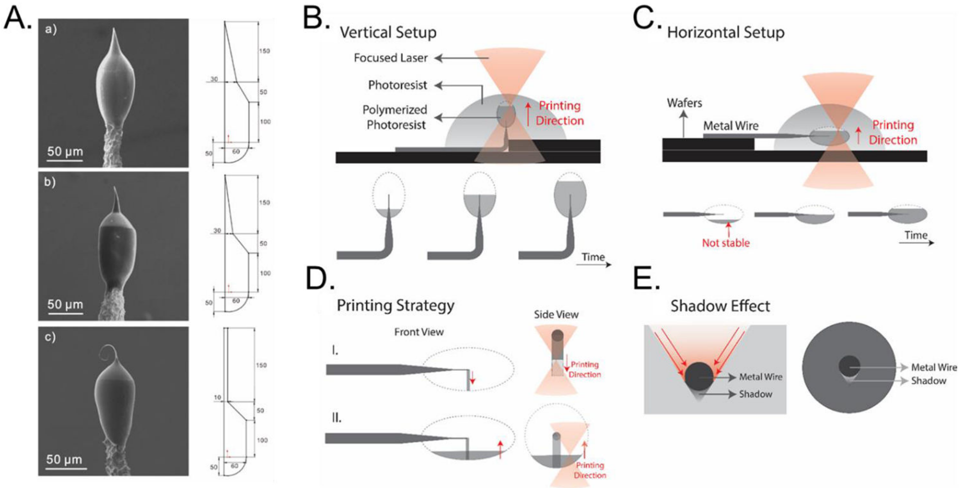


Figure 3.

Limitations for 2-photon lithography. (A) Curling may occur at a high aspect ratio structure during pyrolysis. (a)-(c) are example SEMs and designs of 3D printed tips. (B-E) Illustration for the vertical and horizontal stage setup options: (B) vertical setup and (C) horizontal setup. (D) A proposed strategy for horizontal setup to connect the structure at the beginning of the printing process, and (E) illustration of shadow effect.

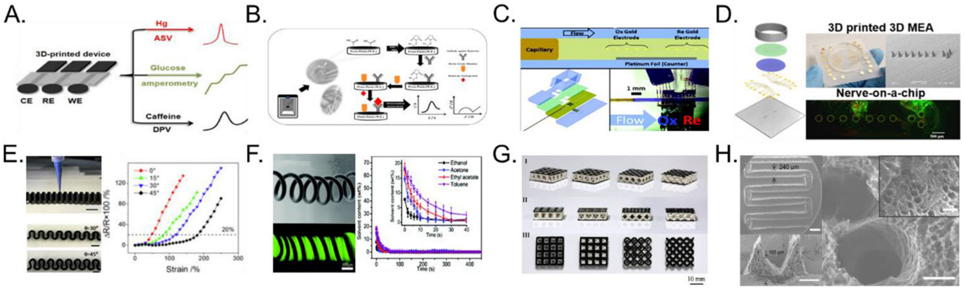


Figure 4.

3D printed devices and sensors for applications. (A) A 3D printed electrochemical cell that contains a 3-electrode system for different analyte measurements.[35] (B) 3D printed electrodes as a platform for Immunosensor buildup to detect a virus.[36] (C) Embedded dual working electrode arrays with microfluidic devices fabricated by additive manufacturing.[37] (D) 3D microelectrode arrays for nerve-on-a-chip device.[38] (E) 3D printed wavy electrodes by PDMS-CNT composite ink with good stretchability.[40] (F) Multifunctional helical liquid sensor by solvent-cast 3D printing.[41] (G) Multi-material 3D printed piezoelectric nanocomposite lattices with different geometry designs for pressure sensing.[42] (H)SEM images of direct laser writing for flexible piezoresistive sensor arrays fabrication.[43] Scale bar for the top right is 500 µm, the top left is 20 µm, the bottom left is 100 µm, and the bottom right is 5 µm. Panels A, B, G and H were reprinted by permission from Elsevier, Panels C and F were from Royal Society of Chemistry, Panel D from American Chemical Society. Panels E was reprinted by permission from Wiley.